

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No: 37697-0063

Applicant(s): Edward W. MERRILL *et al.*

Confirmation No.: 7398

Serial No.: 10/197,209

Examiner: Susan W. Berman

Filing Date: July 18, 2002

Group Art Unit: 1711

Title: RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR
WEIGHT POLYETHYLENE PROSTHETIC DEVICES

DECLARATION UNDER 37 C.F.R § 1.131

THIS DECLARATION IS TO BE MAINTAINED UNDER THE LIMITED ACCESS

PROVISIONS OF 37 CFR § 1.612; MPEP § 2309.03

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We, Edward W. Merrill, William H. Harris, Premnath Venugopalan, Murali Jasty, Charles R. Bragdon, and Daniel O. O'Connor, do hereby declare as follows:

1. We understand that the claims in the captioned application have been rejected over U. S. patent No. 6,281,264, which lists January 20, 1995 as the earliest filing date. All dates on the attached Exhibits have been masked out.

2. We submit this declaration, based on our personal knowledge to explain the process leading to the inventions disclosed in U. S. application Serial No. 10/197,209 that relate to orthopedic preformed materials and polymers, articles and the like that comprise polymers cross-linked by irradiation and heated to or above the melting point of the polymer, and methods of making same. The application also relates to processes of preparing prosthetic bearing comprising the steps of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state.

3. Wear of polyethylene and the incidence of osteolysis became known during mid-1980's. The realization was that the osteolysis was related to the formation of very small polyethylene particles through wear. In order to improve wear resistance of polyethylene and to prevent the formation of fine polyethylene particles, we carried out

inventive activities and designed and carried out various experiments prior to January 20, 1995. All dates on the attached Exhibits have been masked out.

Cross-linking by Irradiation in a Molten State to lower crystallinity and Preserve the Entangled State

4. Prior to January 20, 1995, we developed several ideas to lower crystallinity and preserve the highly disordered entangled state of the ultra-high molecular weight polyethylene (UHMWPE) in order to solve the wear problem (see Exhibit 1). One embodiment that we developed was to cross-link the polyethylene in the molten state by use of irradiation so that the polyethylene could not revert readily to the chain folded state, which was preferred at the time. This embodiment is memorialized in item C of Exhibit 1. The process also is disclosed in U.S. Serial No. 08/600,744, filed February 13, 1996, and issued as U.S. Patent No. 5,879,400 (the '400 patent) (see, for example, Column 6, lines 55-67, and Example 1), U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 25, Example 1), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 33-34, Example 1).

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6. Prior to January 20, 1995, we continued conducting melt-irradiation (MIR) experiments at Mr. Kenneth Wright's laboratory (the High Voltage Research Laboratory (HVRL), located in building N-10 of M.I.T. at 155 Massachusetts Avenue, Cambridge, MA 02139. Mr. Kenneth Wright was responsible for the day-to-day operation and

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7. Also, prior to January 20, 1995, we conducted a thermal analysis of the irradiated UHMWPE specimens, as described in paragraph 9, by use of DSC. This DSC method is used to determine melting and crystallization temperatures as well as the energy input required to melt and energy output generated during crystallization. The energy required to melt is then used to quantify the degree of crystallinity.

Six polymer samples, as described in paragraph 9, also were irradiated in sealed pans for crystallinity analysis. The samples were heated to melt and irradiated while in a molten state. A copy of Premnath Venugopalan's laboratory note book page numbers 8-9 is attached as Exhibit 3 (see Expt 1 and Expt 2). Thus, prior to January 20, 1995, we have practiced the process of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state. The DSC testing on the polyethylene samples that were irradiated in a molten state was conducted. Crystallinity levels had dropped to 37.77% (printed as 37.8%) for the sample given a 20 Mrad radiation dose. Copies of the corresponding DSC data sheets are attached as Exhibit 4 (marked as 'data-6'). Crystallinity data from unirradiated GUR415 bar stock was used as control. Irradiation dose (20 Mrad), temperature (125.51, printed as 125.5) and crystallinity data (37.77%, printed as 37.8%) from this work are presented in a patent application that became the '400 patent (see, for example, Table 1 on column 9 of the '400 patent), in the '313 application (see, for example, Table 1, page 27), and the '638 application (see, for example, Table 1, page 35).

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ESR results indicated no detectable free radicals in melt-irradiated polyethylene, whereas the control polyethylene that was irradiated at room temperature without concurrent or subsequent melting showed the presence of free radicals. The absence of free radicals in the melt-irradiated polyethylene indicates that any further oxidative degradation would be avoided, and thus the material was suitable for use in medical prostheses. See Exhibit 5 for ESR spectra from an experiment conducted prior to January 20, 1995. The ESR spectra show samples irradiated at room temperature contain free radicals; whereas, the samples irradiated at 175°C do not have any detectable free radicals.

Swell Ratios indicated that the melt-irradiated polyethylene was highly crosslinked and did not allow dissolution of polymeric chains, while unirradiated polyethylene dissolved completely, which signifies lack of cross-linking in the unirradiated polyethylene. See Exhibit 6 for swell test results of an experiment conducted prior to January 20, 1995. Swell test data shows control specimens dissolve completely within 24 hours in DecalinTM at 150°C.

9. The above testing confirmed that we had invented, among other things, (1) methods of making an improved prostheses by combining melting and irradiating to cross-link UHMWPE, and (2) improved prostheses that were the result of these processes. These prostheses are wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

Cross-linking by irradiation at room temperature and subsequent melting

10. Prior to January 20, 1995, we also developed another embodiment to preserve the highly disordered entangled state of the UHMWPE in order to solve the wear problem (see item b of Exhibit 1). The embodiment involved cross-linking the polyethylene in at room temperature ('cold irradiation') by irradiation and subsequent melting. The process is referred to as Cold-irradiation and Subsequent Melting or "CISM " and is disclosed in U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 39, Example 8), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 47-48 , Example 8).

11. According to this embodiment, UHMWPE is irradiated at room temperature to cross-link and subsequently the irradiated UHMWPE is heated above the melting point of about 135°C and then cooled. This process subsequently referred to as cold irradiation and subsequent melting or "CISM", meaning irradiation of UHMWPE at about room temperature and then heating the irradiated UHMWPE above the melting point and resolidifying.

12. Prior to January 20, 1995, we had a number of UHMWPE specimens irradiated at room temperature at Mr. Kenneth Wright's laboratory. A copy of Mr. Wright's laboratory logbook pages number 120-121 containing a log of irradiation work done prior to January 20, 1995 is attached as Exhibit 2. The experiment (Marked as Irradiation Experiment 1) and the process including radiation doses used are recorded in lab note book no. 2, page no. 8. A copy of the laboratory note book page number 8, which is attached as Exhibit 3.

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The above testing confirmed that we had developed (1) methods of making improved prostheses using the CISM method to cross-link UHMWPE, and (2) improved prostheses that were the result of the process. These prostheses would not be a source of the fine particles that would result in bone resorption as was the case with the prior art UHMWPE prosthesis. Subsequent testing also confirmed that the elimination of free radicals was provided by this method. Thus, prior to January 20, 1995, we conceived and reduced to practice the CISM invention, that is irradiation of UHMWPE at room temperature and subsequent melting, as described in item b of Exhibit 1.

14. The above testing confirmed that we had invented, among other things, (1) methods of making an improved medical implant having bearing surface comprising a solid polyethylene by irradiating to cross-link UHMWPE and subsequent melting, and (2) improved medical implants. This medical implant would be wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false

statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

April 14, 2004
Date

Date

Date

Date

Date

Date

Edward W. Merrill
Edward W. Merrill

William H. Harris

Premnath Venugopalan

Murali Jasty

Charles R. Bragdon

Daniel O. O'Connor

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We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false

statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date

Edward W. Merrill

Date

William H. Harris

3-5-04 (3 May 04)

Date



Premnath Venugopalan

Date

Murali Jasty

Date

Charles R. Bragdon

Date

Daniel O. O'Connor

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No: 37697-0063

Applicant(s): Edward W. MERRILL *et al.*

Confirmation No.: 7398

Serial No.: 10/197,209

Examiner: Susan W. Berman

Filing Date: July 18, 2002

Group Art Unit: 1711

Title: RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR
WEIGHT POLYETHYLENE PROSTHETIC DEVICES

DECLARATION UNDER 37 C.F.R § 1.131

THIS DECLARATION IS TO BE MAINTAINED UNDER THE LIMITED ACCESS

PROVISIONS OF 37 CFR § 1.612; MPEP § 2309.03

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We, Edward W. Merrill, William H. Harris, Premnath Venugopalan, Murali Jasty, Charles R. Bragdon, and Daniel O. O'Connor, do hereby declare as follows:

1. We understand that the claims in the captioned application have been rejected over U. S. patent No. 6,281,264, which lists January 20, 1995 as the earliest filing date. All dates on the attached Exhibits have been masked out.

2. We submit this declaration, based on our personal knowledge to explain the process leading to the inventions disclosed in U. S. application Serial No. 10/197,209 that relate to orthopedic preformed materials and polymers, articles and the like that comprise polymers cross-linked by irradiation and heated to or above the melting point of the polymer, and methods of making same. The application also relates to processes of preparing prosthetic bearing comprising the steps of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state.

3. Wear of polyethylene and the incidence of osteolysis became known during mid-1980's. The realization was that the osteolysis was related to the formation of very small polyethylene particles through wear. In order to improve wear resistance of polyethylene and to prevent the formation of fine polyethylene particles, we carried out

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Cross-linking by Irradiation in a Molten State to lower crystallinity and Preserve the Entangled State

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Date

Edward W. Merrill

Date

William H. Harris

Date

Premnath Venugopalan

4/22/04

Date

Murali Jasty

Murali Jasty

4/21/04

Date

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Date

Daniel O. O'Connor

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No: 37697-0063

Applicant(s): Edward W. MERRILL *et al.*

Confirmation No.: 7398

Serial No.: 10/197,209

Examiner: Susan W. Berman

Filing Date: July 18, 2002

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The above testing confirmed that we had developed (1) methods of making improved prostheses using the CISM method to cross-link UHMWPE, and (2) improved prostheses that were the result of the process. These prostheses would not be a source of the fine particles that would result in bone resorption as was the case with the prior art UHMWPE prosthesis. Subsequent testing also confirmed that the elimination of free radicals was provided by this method. Thus, prior to January 20, 1995, we conceived and reduced to practice the CISM invention, that is irradiation of UHMWPE at room temperature and subsequent melting, as described in item b of Exhibit 1.

14. The above testing confirmed that we had invented, among other things, (1) methods of making an improved medical implant having bearing surface comprising a solid polyethylene by irradiating to cross-link UHMWPE and subsequent melting, and (2) improved medical implants. This medical implant would be wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false

statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date

Edward W. Merrill

Date

William H. Harris

Date

Premnath Venugopalan

Date


Murali Jasty

Date

5/19/04

Date

Charles R. Bragdon



Daniel O. O'Connor

EXHIBIT - 1

BULK CROSS-LINKING FOR IMPROVED UPE PROPERTIES

↳ starting

BASIC MOTIVATION :-

It is clear that as mol. wt. of PE increases, its abrasion resistance increases. Further as hypothesized by Prof. Merrill, the increase in entanglements should reduce wear. ~~Both ways~~ ^{There seems to be an effort at} increasing the resistance of PE chains to ~~being~~ ^{being} pulled out of the bulk.

Hence, the following treatments ~~are~~ are being considered as ways to increase the resistance faced by PE chains against being pulled out:

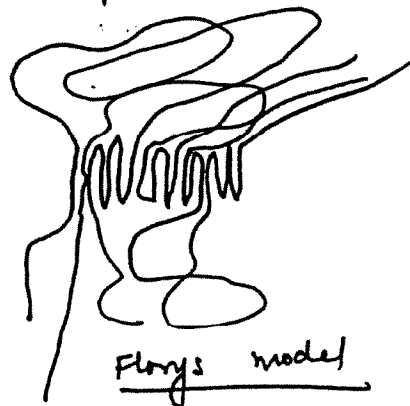
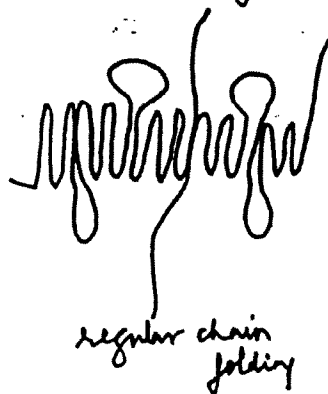
(a) Heat and rapid cooling: Heat the polymer to a completely disordered ~~state~~, highly entangled state and then suddenly cool it ~~in order to~~ trap it in that state.

This may be possible with 10 μ thick films dipped into liq. N₂ but is not possible for larger specimens (Researchers have used several 100 to 100,000 °C/min). Further there are problems of differential crystallization at different positions and problem of strain concentrations.

(b) Crosslink as solid, melt, recrystallize: Irradiating the polymer as a solid will mean ~~less~~ ^{crosslinking} ~~crosslinking~~ at the crystalline zones but higher crosslinking in the amorphous zones (more mobile chains can ~~move~~ jump more to connect at different places). Melting & recrystallizing these will probably again lead to the original crystal structure ~~with~~ ^(though with reduced crystallinity) ~~though~~ and selective segregation of crosslinks into the amorphous regions. This is expected to be more wear resistant since molecules in the tie regions may be interconnected & crosslinked. Promises to be useful if (a) inter crystalline region slip is

important during wear (to) if loss in hardness is not crucial.

(c) Crosslink as melt, recrystallize: More reduction in crystallinity expected with uniform crosslinking (much more than in x-linking of the solid). More likely that chain-folding in the Flory sense, ^{will occur} where ~~chains do~~ ~~not fold so~~. Instead of one chain folding repeatedly, ~~several~~ many chains will fold in a given region. Hence ~~the~~ the amorphous region will have more interconnected regions, x-link points & longer loops.



(d) Crosslink the solid:

~~the~~ Hardness of original UPE is retained and hopefully there will be ~~more~~ selective crosslinking in the amorphous regions.

Questions/Concerns:

① Degradation vs. Crosslinking

Mol wt ↓
Xstallinity ↑
Wear ↑
Free radicals
(long term existence)

Extent ?

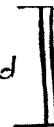
② Crosslinking vs. Crystallinity

↓
decreases as
xlinking ↑ (if recrystallized)

③ Crosslinking vs. Crystal structure

Ideas:

① Crosslinking by irradiation of
Hylamer after it has been processed
and no recrystallization.



⇒ Highest crystallinity
+
Crosslinking.

② Study crosslinking in HDPE instead to see
extent of unlinking, degradation etc.

IRRADIATED SPECIMENS
FROM ZIMMER

$$\begin{aligned}
 * \quad 1 \text{ Mrad} &= 10^4 \text{ ~~erg~~ } = 10^8 \frac{\text{erg}}{\text{g}} \\
 \frac{10^{-7} \text{ J}}{\text{erg}} &= \text{erg} \\
 10^{-2} \text{ erg} &= \text{rad} \\
 &\downarrow \\
 &\text{J/kg} \\
 \hline
 100 \text{ rad} &= \text{J/kg} \\
 1 \text{ Gray} &= 1 \text{ J/kg} = \frac{10^{17} \text{ erg}}{10^3 \text{ g}}
 \end{aligned}$$

Data 2

DSC RESULTS: [Effect of freezer-milling and Effect of crosslinking by irradiation]

Sample	T _{m1} (°C)	T _c (°C)	T _{m2} (°C)	% Cryst 1	% Cryst. 2	Difference in Crystallinity	Arg. Lamellar thickness I	Arg. lamellar thickness 2
(GA)								
GUR 415 - CONTROL	135.83	122.80	127.52	62.91	46.42	16.49	2.91 x 10 ⁻⁶	1.51 x 10 ⁻⁶
(MFL)								
GUR 415 - FREEZER-MILLED - 10 min.	121.86	154.11	104.47	0.28 So low a crystallinity?	0.57 Again low order after heating?	-0.30	1.15 x 10 ⁻⁶	0.653 x 10 ⁻⁶
BAR - CONTROL	127.39	121.71	126.57	52.92	46.37	6.55	1.52 x 10 ⁻⁶	1.44 x 10 ⁻⁶
BAR - 10 Mrad	130.53	127.95	119.05	54.02	45.29	8.73	1.84 x 10 ⁻⁶	1.02 x 10 ⁻⁶
BAR - 20 Mrad	131.05	129.48	119.78	54.95	41.69	13.26	2.05 x 10 ⁻⁶	1.05 x 10 ⁻⁶

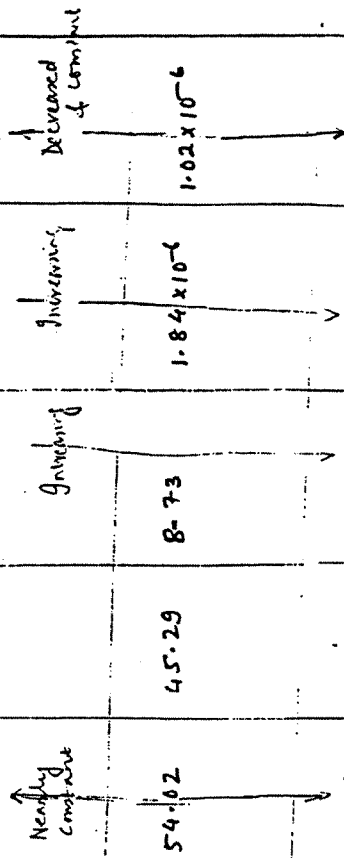


EXHIBIT - 2

1.45

COOP COMPUTATION BOOK

NAME	NUMBER
KEN WRIGHT	1

Course F-13-2.1

Used from..... to.....

HARVARD COOPERATIVE SOCIETY
1400 MASS. AVE., CAMBRIDGE, MASS. 02138

TECH. COOP
84 MASS. AVE. CAMBRIDGE, MASS. 02139

Murill	10	2.5	41	15	1.1	75	1.3	1.25×10^6
Bertrand	1-2	2.5	39	-	-	90	-	1.25×10^6 11
PEO collagen Perez	1-9	2.5	62	24	1.1	430	1.3	2×10^6
Collagen on millipore filter	1-6	-	-	-	-	-	-	-

TSC Litho Liquid N₂

PMMA	1	2.5	20	8.1	1.1	40	3.2	2.5×10^5
4" dia discs 1/2" thick	2	-	28	10.2	-	-	-	3×10^5
	3-5	-	26	-	-	-	-	-
	6-8	-	-	-	-	-	-	-
	9-10	-	17	6.8	-	58	-	2.5×10^5
3/8" thick	11	2.0	33	10.2	-	90	-	3×10^5
	12-15	-	39	11.9	-	90	-	5.5×10^5

1-3 Gonter	1-18	2.5	39	15	1.1	400	1.3	1.25×10^6
4- 9chs of PEO ⁺ different	1-13	-	-	-	-	-	-	3.2×10^6
concentration	2-8	-	-	-	-	200	-	5.5×10^6 11

Thin Alms Polyurethane	1-3	-	30	12	-	100	1.3	10^6
Mumser Markth 4-6	-	-	-	-	-	-	-	7.25×10^6 11
3-2108, Rm 35-332	-	-	-	-	-	-	-	-

Small (6.5cm Premnath Venugopal)	1-6	2.5	39	15	1.1	75	1.3	1.25×10^6
dia) cups	2-8	-	-	-	-	-	-	-
	3-6	-	-	-	-	-	-	11
	4-6	-	52	20	-	-	-	111
	5-6	-	63	24	-	-	-	2×10^6 111
	6	-	-	-	-	-	-	111
	7	-	-	-	-	-	-	111
	8	-	-	-	-	-	-	111

Slush	1-4	2.5	33	13.6	-	430	1.3	10^6 11
	5-8	-	-	-	-	-	-	11
	9-12	-	68	27	-	-	-	2×10^6

Various strips	1-6	-	38	15	-	125	-	1.25×10^6
core ten	1-5	-	-	-	-	-	-	-
	1-3	-	-	-	-	-	-	11

No overlay (sufficient liquid overlay)

$$2.25 \times 10^6$$

Glass covers overlays

2 Pb over central area

No Pb

2 overlays

$$2.25 \times 10^6 \text{ #Hatched over}$$

$$2.5 \times 10^6$$

2

$$2.25 \times 10^6$$

$$2.5 \times 10^6$$

$$2.10$$

$$2.2 \times 10^7$$

$$2.3 \times 10^7$$

$$2.4 \times 10^7$$

$$2.5 \times 10^7$$

$$2.5 \times 10^6$$

2 overlays

$$2.5 \times 10^6$$

$$2.25 \times 10^6$$

$$2.5 \times 10^6$$

1.8 MP may be slightly less than 5

$$2.5 \times 10^6$$

Polyethylene + Guestron Schmitt
Acetone, water

1-2 26 50 20 1.1

6.5 6.5 x 10⁶

PEO in Petri dishes Stephanie
Prof. Cima Lapina

1-10 26 30 12 1.1 2.50

1.3 20⁶ 11

Stephani Lapina 1-15 - 60 24 - 340

- 2 x 10⁶

3-7115 1-20 - - - - 440

- -

354-7489

Back - wetted &
dried

Chat Cooke 1 26 60 24 1.1 160

1.3 2 x 10⁶

2 - - - - -
3,4 - - - - - 200

- - - - - 11

1944 6 x 6 (1-16) Ken Brecher - 8 2.1 17.6 6.8 1.0 140

3.2 2 x 10⁶

(Fractal) B.U. 7-12 - 17.5 6.1 - -

17-32, Dept of Astronomy 180

725 Comm. Ave 13-32 170

Cyber + other shops 02215 35-42

353-2625 - 8.5

PTFE + Polyethylene
PRO*

1-3 1 37 18 1.1 140

1.3 1.25 x 10⁶

PEO in Petri dishes sec

1-20 1 30 12 1.1 440

1.3 10⁶ 11

above

Prof. Cima 1-15 - 60 24 - 360

- 2 x 10⁶

Polyethylene
over hot plate

Premnath Varugopalan 1-4 2.8 70 30. 85

- 2.5 x 10⁶

1-3 - - - - -

- - 11

1-2 - - - - -

- - 11

1 - - - - -

- - 11

- - - - -

- - 11

See above

Stephani Lapina 1-15 2.6 30 12 1.1 355

1.3 10⁶

Polyethylene
1-4 hot plate

Premnath Varugopalan 1-8 2.6 37.5 15 - 135

1.3 1.25 x 10⁶

1-3.5-7 52

- 1.25 x 10⁶ 1111

1-2.5-6 2.8 52 24 - 105

- 2 x 10⁶ 11

1.5 - - - - -

- - - 111

1 - - - - -

- - 111111

PEO soln ~~PTFE~~ PTFE Schmitt

1-20 } 2.6 37.5 15 - 165

1.3 1.25 x 10⁶

Polyethylene Premnath

1-4.6-6 } 2.6 37.5 15 - 165

* small beads * 1-6*

1-4.1-5-7 } - - - - -

1-4.1-4-9 } - - - - -

1-3.1-4-9 } - - - - -

1-3.1-3-9 } 2.75 47 20 - -

1-4.1-2-9 } - - - - -

1.1-1-1-1 } 2.4 - 100

- - - - -

- - - - -

- 1.06 x 10⁶

- 1.25 x 10⁶

186 L Ni

2nd day

5.2×10^6

Turned over for 2nd run

1 discharged

Petri dishes in glass covers

5.2×10^6

5.10^7

5.2×10^7

5.5×10^7

5.5×10^7

5.2×10^6

5 5.2 1st run hot plate jammed before irradiation - adjusted and passed through

$5.9.8 \times 10^6$

$5.19.8 \times 10^6$

$5.29.5 \times 10^6$

$5.49.8 \times 10^6$

$5.2.5 \times 10^6$

$5.3.75 \times 10^6$

5.5×10^6

5.10^7

5.2×10^6

5.5×10^7

EXHIBIT - 3

Student's Name

Date

8

Subject

Instructor's Name

Irradiation
Studies.

→ e⁻ beam
at HVRL, MIT.

✓ Kenneth A. Wright.

Student's Name

Date

8

Subject

Instructor's Name

EXPT (1) → Irradiation of solid polymer (UPE) from bar stock

~~Irrad/RT/DSC/ANAL/PHOTO~~

Set 1

↓
12 samples
of thickness of a
few microns kept
between two slides

RT
1.0 MRad (each)
2.5 MRad
5.0 MRad
10.0 MRad
20 MRad
50 MRad

↓
This was for
studies under
polarizing
microscope
at MGH

↓
Result → all

showed spherulites
on melting & cooling
under microscope

Set 2

↓
6 samples in
DSC pans

RT
1.0 MRad
2.577 " "
5.0 " "
10.0 " "
20.0 " "
50.0 " "

↓
DSC Runs done
& results in
the file (# 3)

Subject

Instructor's Name

EXPT.

(2) Irradiation of barstock while a melt.

9 mm / 175°C / Air / No follow HT / PANG

FHT

6 Samples → 1.0, 2.5, 5, 10, 20, 50 Mrads.

at temp $> 150^{\circ}\text{C}$

Range (155 to 180°C approx.)

Heating → Sample heated ~~approx~~ ~~once~~ intermittently.

Heated → 1.0 Mrad → Heated → 2.5 Mrad

10 Mrad ← Heated ← 5.0 Mrad ← Heated

Heated → 20 Mrad → Heated → 35 Mrad

Heated
50 Mrad

Samples placed on a heated Al plate (sink).

Analysis → In file #3.DSC Data:

Dose	mg
1	9.732
2.5	11.433
5	9.540
10	9.061
20	10.133
50	11.638

There was some confusion because the heating ~~exposed~~ ~~damaged~~ the marks on the pans.

Weights were correlated by measuring

again. Fortunately, the weights were well distributed and each far apart from another.

Student's Name

Date

Subject

Instructor's Name

EXPT. 3: Irrad. / 75 C / N₂ atm / NO follow-up HT / VIALS
→ FUHT

Samples :- Barstock (from surface) → constant radius. ~~4~~
Samples 4 no. 2.5 to 3 cm radii

4 samples → 2.5, 10, 20, 50 MRad

Method :- Thin strips in vials.

Vial filled with N₂ as in heat treatments.

Heater used this was small enough to fit
under generator outlet
(heater provided by Prof Merrill)
cooling in air (Room temp.)

Sample left in ^{vial with} N₂ atmosphere at R.T after irradiation.
for > 5 days

Analysis

Student's Name

10

Subject

Instructor's Name

EXPT 4: Irrad/175C/Air/NO FUHT/VIAL

Samples : Bar stock (b/w 2.5 to 3 cm radial distance)

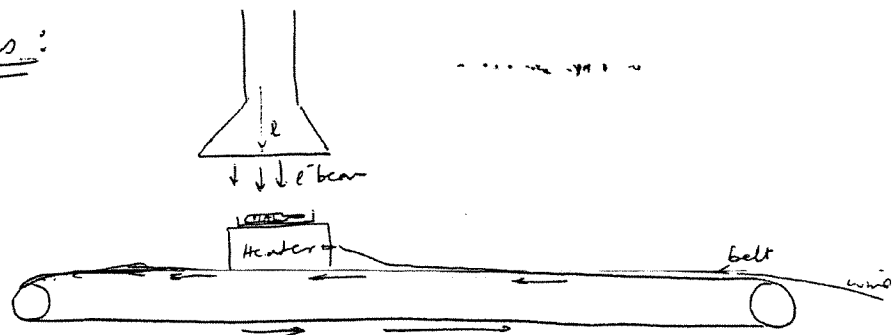
4 Samples \rightarrow 2.5, ^(9.8)~~10~~, ^(9.8)~~20~~, 50 M Rad.

Method : (As in previous page)

Analysis

: E.79x3

Apparatus:



Student's Name

Date

10

Subject

Instructor's Name

EXPT 5: Irrad / RT / N₂ / NO FUHT / VIALSample → Same as last page.Method → Same as last page.~~EXPT 5~~

	Time	MRad
①	2.5	"
②	0.8	"
③	10.8	"
④	50	"
⑤		
⑥		
⑦		
⑧		
⑨		
⑩		

EXHIBIT - 4

E-IRRADIATION OF
THE MELT.

E-IRRADIATION OF THE MELT

Procedural Details:

The following experiment was performed at HVRL, MIT. The Points to be noted ~~steps~~ were as follows:

- (1) Since the hot plate would not fit under the Van de Graaf generator, the specimens ^{in DSC pans} were placed in between two petridishes and laid on a metal plate acting as a heat sink while heating ~~to~~ (supplies heat when placed on the belt).
- (2) The heating was done at intervals ~~between~~ ---...

- Start
- After 1.0 M Rad
- " 2.5 M Rad
- " 3.0 M Rad
- " 10.0 M Rad
- " 20.0 M Rad
- " 30.0 M Rad
- After 40.0 M Rad

- (3) It can be assumed ~~that~~ that approximately the temperature of the specimens was between 150-200°C

NOTE:

- ① Absence of bimodal distribution during crystallization
→ because no crystals during irradiation,
One phase.
(Scission & x-linking is diff. in crystalline regions)
- ② ~~Since~~ lamellar size and crystallinity & T_m decreases,
→ (crystal size)
significant crosslinking occurring
in proportion to scission.
If too much scission compared to crosslinking
→ mol wt would decrease
→ crystallinity & crystal size will increase
(e.g.) HDPE → 60%.

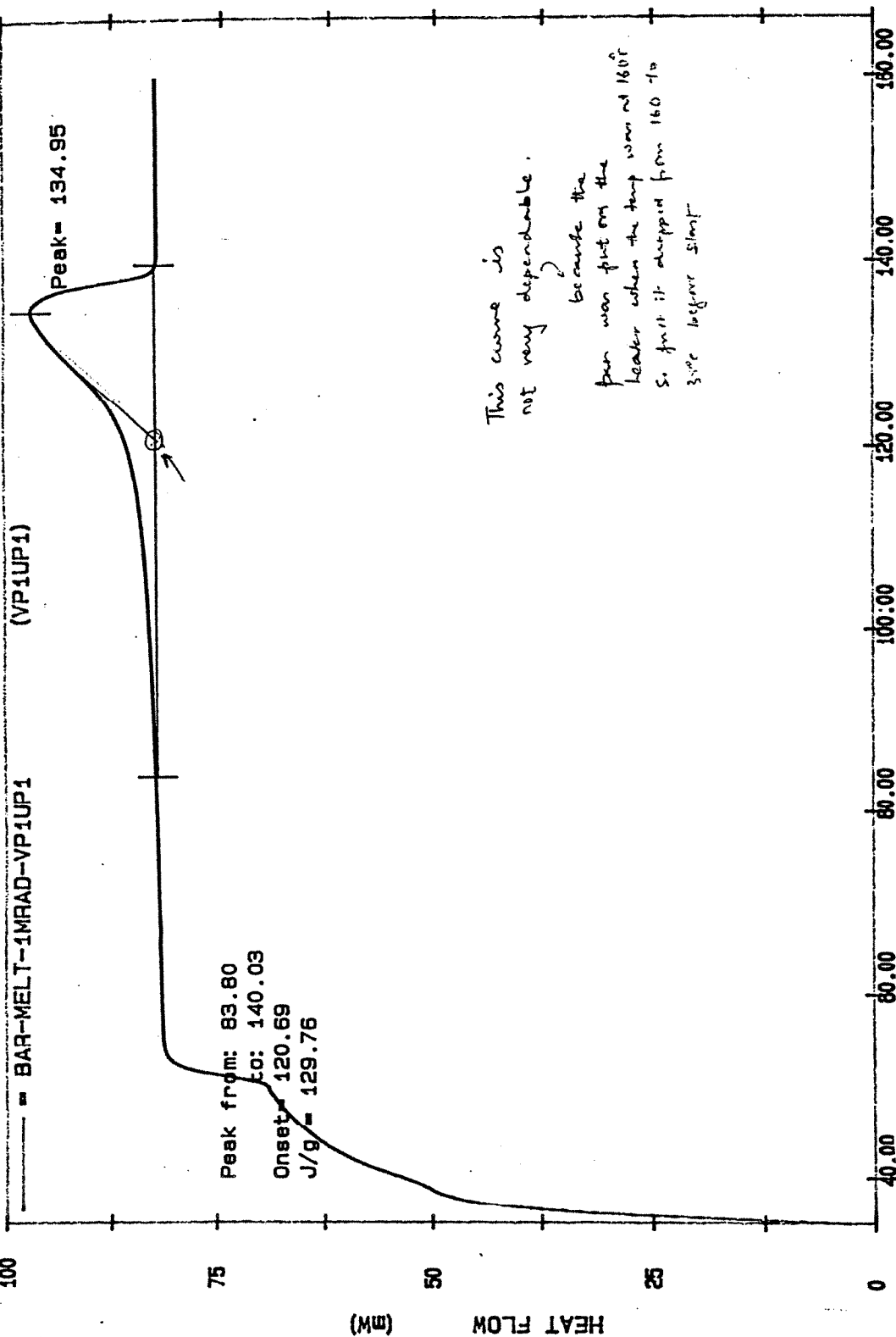
Data 6

Nulad	T_{m1} ($\times 10^{-6}$)	T_c	T_{pade}	T_{m2}	% Crypt 2	Avg. Lowell Amplitude ($\times 10^{-6}$)	Crypt. diff.	Remark.
✓ (1)	120.6	123.93	120.22	170.6	48.20	1.08	-3.38	
✓ (2.5)	120.6	122.93	118.51	119.23	48.11	1.05	-2.26	
✓ (5)	120.6	121.14	117.66	120.22	45.18	1.02	-1.90	
✓ (10)	120.6	118.95	113.68	118.73	32.87	1.01	2.56	No second valley during x-stalling
✓ (20)	118.11	115.06	111.11	117.32	39.09	0.957	-1.31	No second valley during x-stalling
✓ (50)	118.11	105.01	101.18	101.65	32.77	0.748	-1.11	

NOTE: ① Cryptallinity is down below 40% for the first time.
 ② Sudden drop in T_{m2} (as in irradiation of solid P₂) after 20 mRad. (Both T_{m1} & T_{m2})
 ③ T_{pade} consistent but decreasing as rad. dose increased (Both T_{pade} & T_{pade2})
 ④ Original Bar Crypt \rightarrow 55%
 Irrad. well & solidly \rightarrow 30-45%

Lowell Amplitude
to
Cryptallinity

DATA 6



Date: 3:38pm
Scanning rate: 10.0 C/min
Sample Wt: 9.732 mg Path: C:\PE\

PERKIN-ELMER DSC7

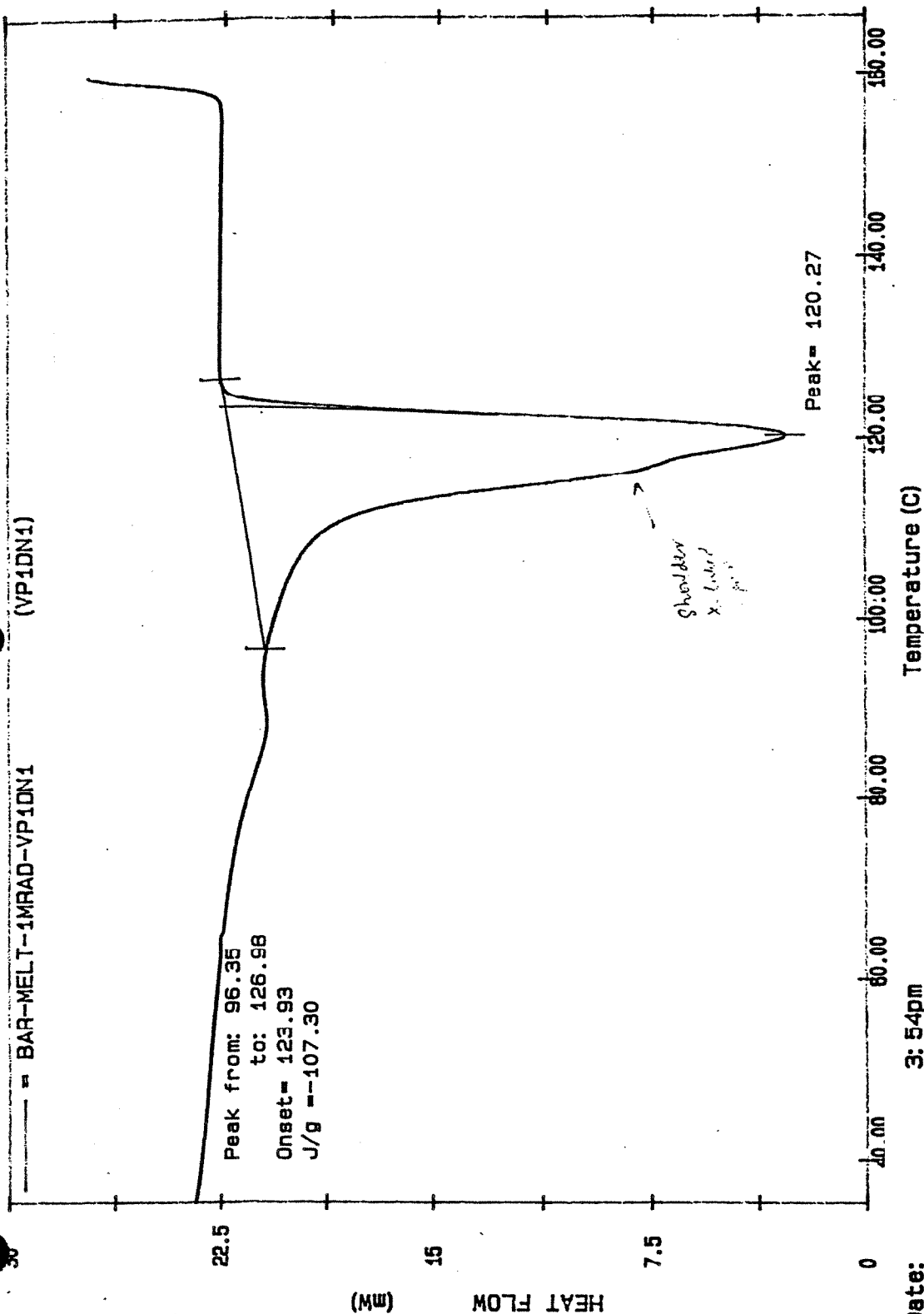
File 1: VP1UP1 PRENT

MISCELLANEOUS DSC SAMPLES

Peak M2	CRIST OFF
132.82	13.80
132.81	24.30
132.81	24.30
132.80	0.00
135.18	27.09
130.26	-0.34
128.80	0.85
132.88	26.43
133.05	1.07
128.20	3.53
128.19	-0.48
128.10	-1.38
128.35	7.22
131.43	1.02
130.28	2.00
130.48	4.30
134.08	18.41
122.58	0.92
128.60	-0.70
124.93	-4.22
132.83	-1.01
132.83	-1.01
132.83	-1.01
127.21	-0.80
127.21	-0.80
127.21	-0.80
128.23	-2.81
132.80	-4.20
133.78	-0.17
123.17	-1.34
117.83	-0.32
134.70	6.85
134.85	9.72
136.00	13.21
135.05	-49.70
133.15	9.11
131.88	7.28
131.18	6.23
130.39	19.03
131.10	19.00
135.85	-3.31
125.83	-2.20
132.48	-1.86
130.05	2.84
128.78	-1.31
117.83	-1.11

BAR-MELT-1MRAD-VP1DN1

(VP1DN1)

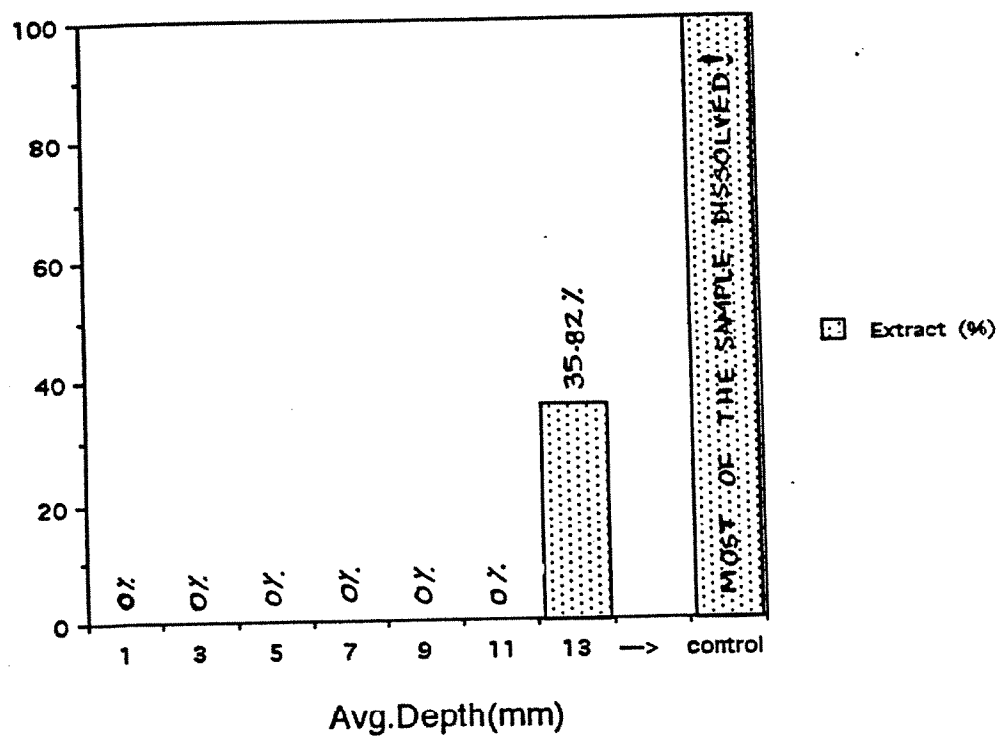


Date: 3: 54pm
Scanning Rate: -10.0 C/min
Sample Wt: 9.732 mg Path: C: \PE\
File 1: VP1DN1 PRENT

PERKIN-ELMER DSC7

EXHIBIT - 5

Extract percent in Decalin at 150 C (Samples from axis of irradiated cup 3)



Results from swelling test in Decalin at 150 C (Samples from axis of irradiated cup 3)

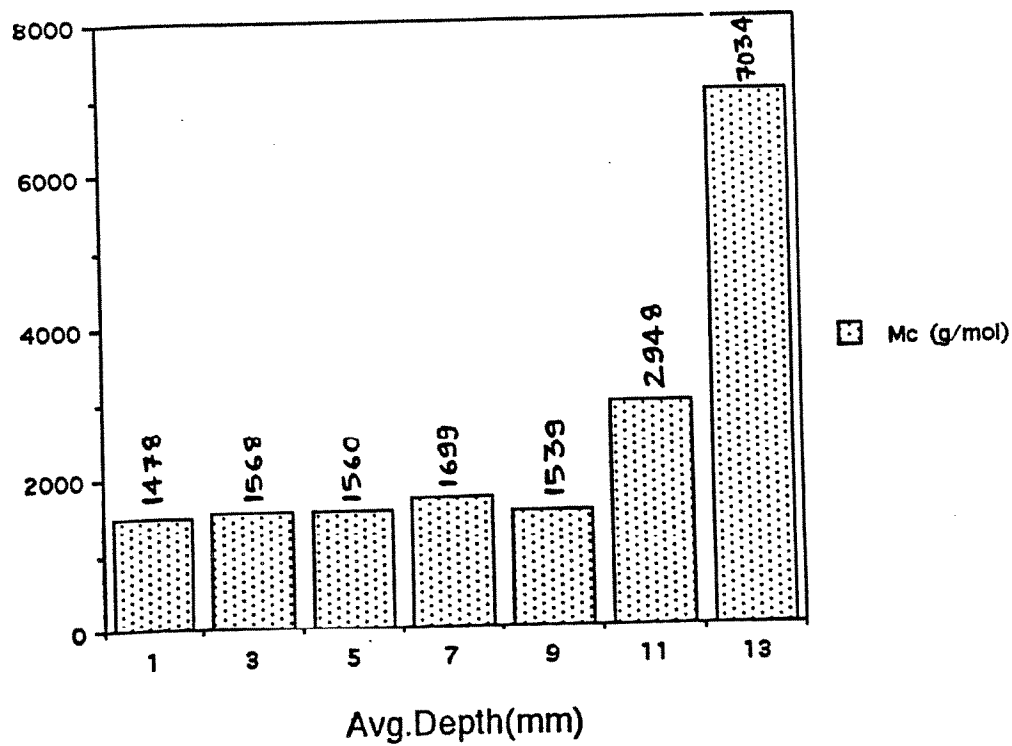
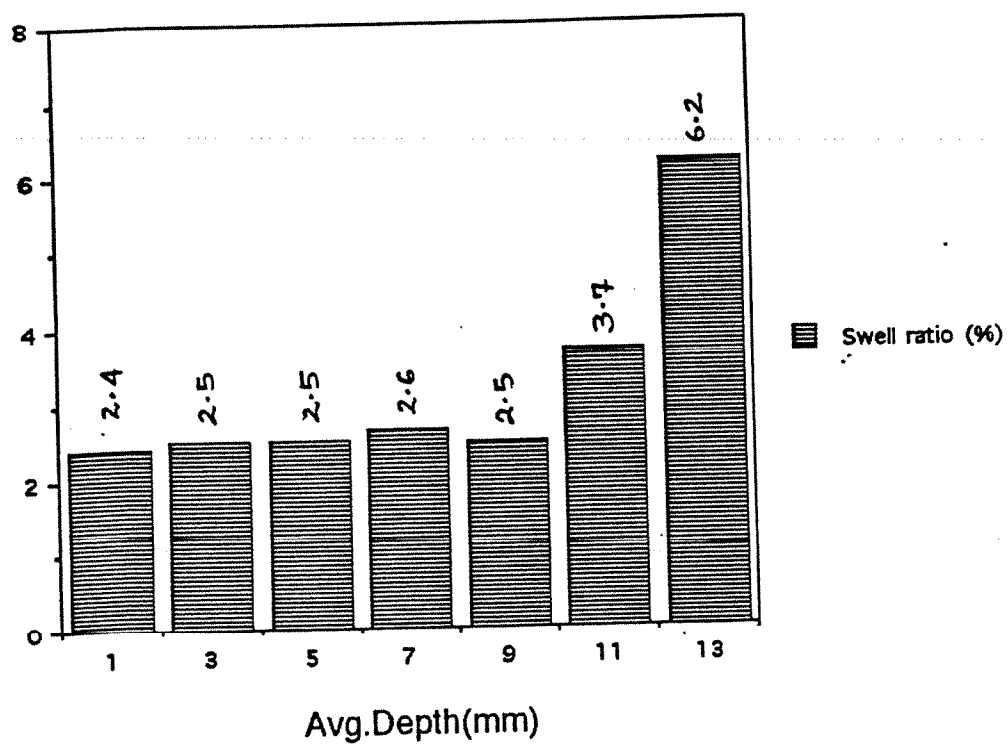


EXHIBIT - 6

EPR Date

Tony Modestino for Remmets

RECORDING CHARTS

Sample: Bar Stock Simulated as Solid at RT
in N₂ atmosphere on Remmets

1 mW

Microwave Power

3×10^4

Receiver Gain

9.74×10^{-1}

Modulation Amplitude

1.28 msec

Time Constant

41 Mhz

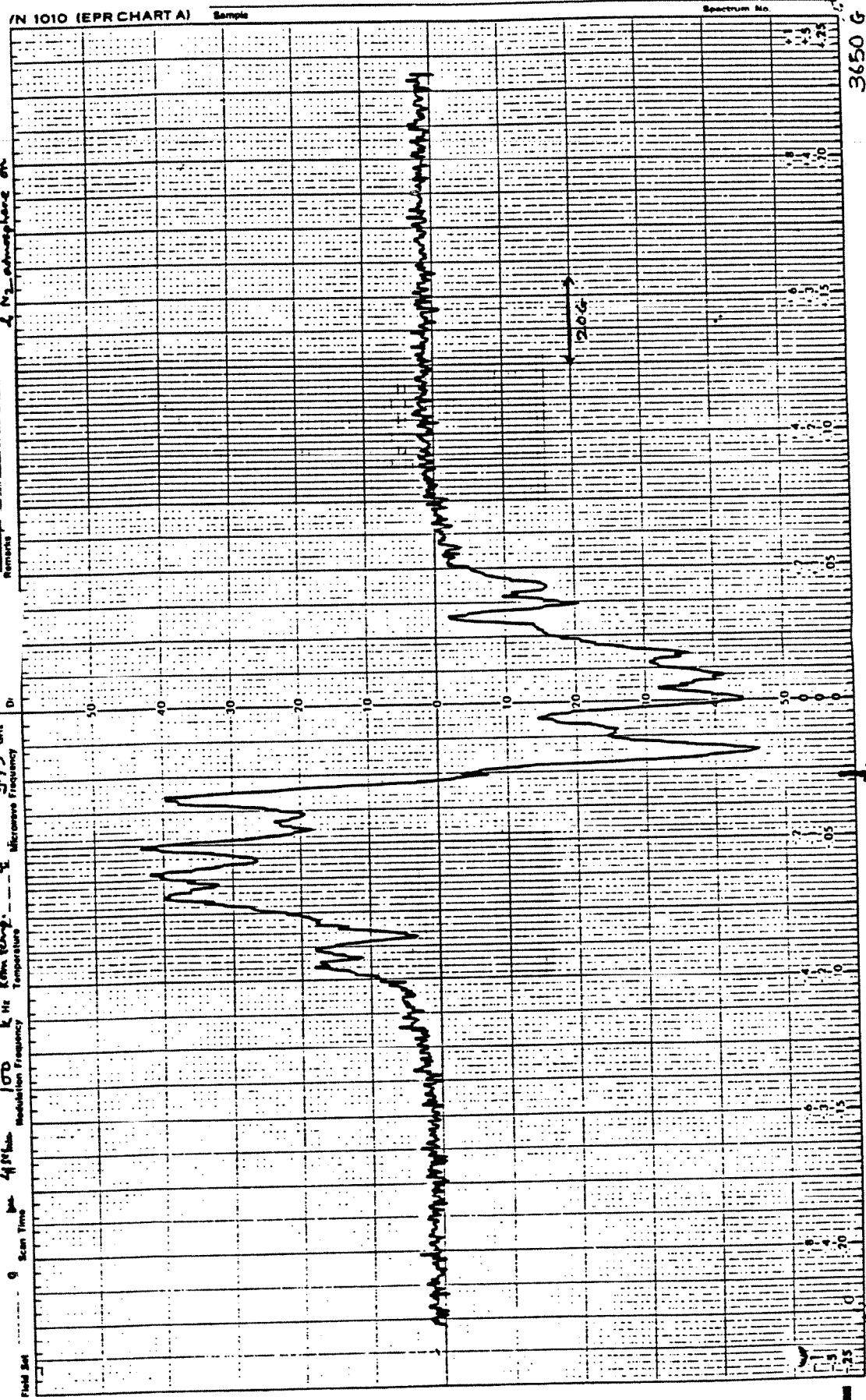
Modulation Frequency

100 KHz

Room Temp.

9.75 GHz

Microwave Frequency

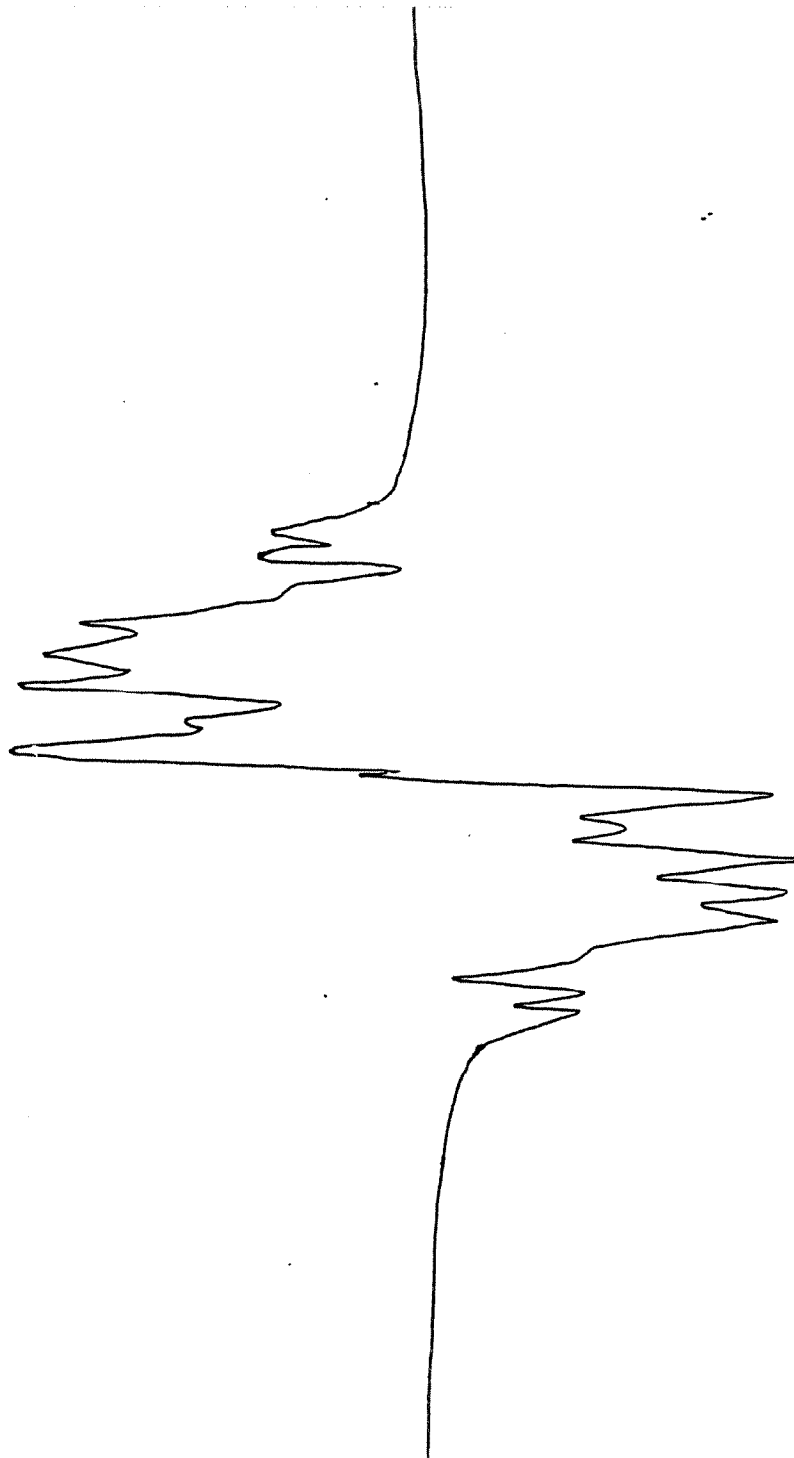


3480.43G
= 19.5G

3350 G

3650 G

MIRROR IMAGE OF ESR SPECTRUM OF UHMWPE IRRADIATED AT RT/N₂ ATM.



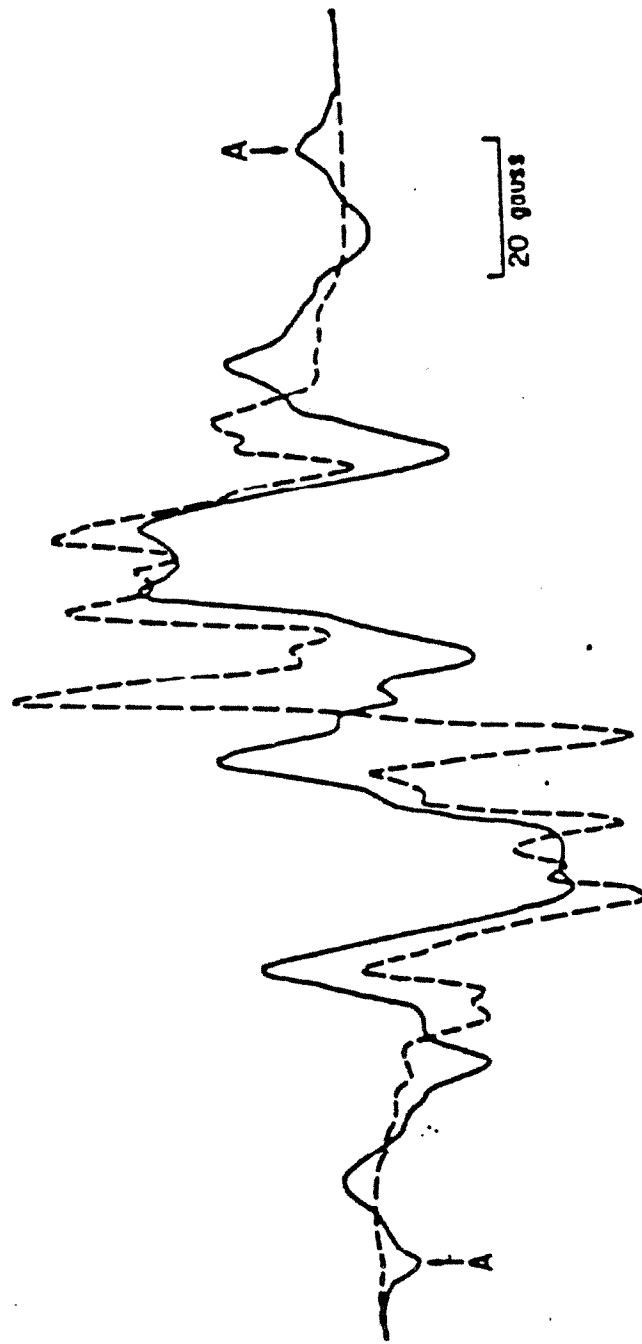


Figure 2. ESR spectra of allyl free radicals (dotted curve) and of mixed alkyl and allyl free radicals after heating to room temperature (solid curve). Decay of alkyl free radicals was calculated from height of peaks marked A.

REFERENCE: D.C. Waterman and M. Dole, J. Phys. Chem., 74 (9), 1970, 1913-1922